

Neutron reflectivity studies of electric field driven structural transformations of surfactants

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Abstract. We employed electrochemical methods together with in situ neutron reflectometry to describe the aggregation of organic surfactant molecules at a solid–liquid interface. The neutron reflectometry allowed us to determine the surface coverage, thickness, roughness and the relative positions of the aggregates. We found that the applied electric field may be used to reversibly manipulate the architecture of the organic molecules: from uniform monolayers to adsorbed hemimicelles. These studies are expected to provide a new insight into the roles played by entropic and electrostatic forces in complex fluids or biomaterials.

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Surfactants are ubiquitous in our daily activities and find use in a host of technologies. Knowledge of the forces that control assembly of surfactant molecules at the solid–liquid interface is vital for traditional fields such as detergency, flotation, oil recovery and tribology [1]. Thin organic films deposited at solid surfaces also find application in the fabrication of optoelectronic devices, sensors, biosensors and chemically modified electrodes [2]. Monolayers and bilayers of phospholipids deposited at solid supports are used as models of biological membranes in biomimetic research [3–5]. It has long been established that the assembly of surfactants at the solid–liquid interface depends on the charge at the solid surface [6, 7]. However, the present understanding of the role played by charge on the interaction of a surfactant molecule with the electrified solid surface is far from being complete.

Electrochemistry provides a unique opportunity to study the affect of the charge on the properties of amphiphilic and ionic surfactants at the charged solid–liquid interface: the charge density at the metal surface may be varied, from about $-30 \mu\text{C}/\text{cm}^2$ to about $40 \mu\text{C}/\text{cm}^2$ [8–13]. This magnitude of charge generates fields on the order of 10^{10} V/m . Such a field interacts with polar molecules at the interface.

We have employed electrochemical techniques together with neutron reflectivity (NR) measurements to directly obtain the density profile for the molecular assemblies covering gold electrode surface. In the separate sets of experiments, we have studied the behavior of three different systems: 4-pentadecyl-pyridine (C15–4Py) [9], sodium dodecyl sulfate (SDS) [8] and dimyristoyl-phosphatidyl-choline (DMPC)-cholesterol mixture [14]. In the present paper we will present our measurements of the negatively charged SDS molecular assemblies under the electric field in the electrochemical cell.

1 Experimental

1.1 Electrochemical characterization

The influence of the electric field on the state of organic films at the gold solution interface can be conveniently described with the help of the charge potential curves. Figure 1 shows the charge density curves determined for gold electrodes covered by films of SDS. The charge densities were

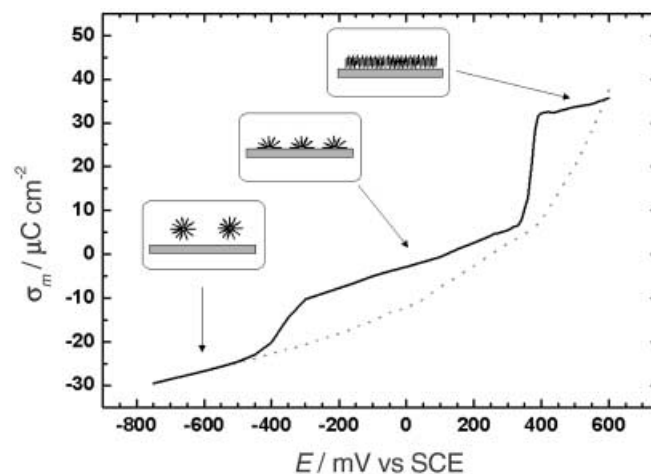


Fig. 1. Charge density of the Au(111) electrode: *dashed line*, film free interface; *solid line* in the presence of 16 mM SDS in the bulk of the solution

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determined using the chronocoulometric technique described in [8–13]. Solid lines show the charge density curves in the presence of the film, dotted lines show charge densities for the film free gold electrode surface. These results, combined with our previous scanning probe microscopy studies [8], show that adsorption of SDS at the Au(111) electrode surface has a two state character. At small or moderate absolute charge densities, the adsorbed SDS molecules aggregate into hemi-cylindrical stripe-like micelles. At large positive charge densities, the hemimicellar aggregates melt to form a condensed film.

1.2 Neutron reflectometry

Monocrystalline quartz substrates (5 Å r.m.s. roughness) were sputtered with thin Cr/Au layers. Their properties were characterized using X-ray and neutron scattering (data not shown). The crystal was mounted on a specially constructed solid-liquid interface cell, described in detail elsewhere [9]. The cell had ports for the counter (gold foil) and reference electrodes (Ag/AgCl, $E = -40$ mV versus SCE). The resistance of the thin film of gold was on the order of a few ohms. The cell was filled with de-aerated, D₂O (99.99%) solutions of SDS with or without 50 mM KClO₄. The experiments were carried out at a temperature of 20 °C at the NG7 reflectometer at NIST, Gaithersburg, USA [8,9]. Neutron

reflectivity measures the normalized intensity of specularly reflected neutrons R as a function of the momentum transfer vector Q_z ($Q_z = 4\pi \sin \theta / \lambda$, where θ is the angle of incidence and λ is the wavelength of the neutrons; 4.75 Å, in our case). The data was reduced taking into account the neutron beam transmission through the quartz substrate and corrected for the background. An inverted geometry, in which the gold coated quartz electrode was above the D₂O phase, was used in our experiments. In this case, the lower medium (D₂O) had a higher scattering length density than the upper one. Under these conditions the reflectivity was approximately unity for Q_z below a critical value $Q_c = 4\sqrt{\pi \Delta \rho}$, where $\Delta \rho$ is the scattering length density difference between the lower and the upper media. Above Q_c , R decays as a function of Q_z and the character of this decay depends on the area-averaged scattering length density profile normal to the interface.

The neutron reflectivity data allows one to determine the scattering length density profile perpendicular to the interface. The surface coverage, thickness, the relative position and the roughness of individual layers can be calculated from the scattering length density profile. Because of the small length-scale and ubiquitous nature of hydrogen in organic assemblies, neutrons are particularly suitable for elucidating structural information regarding these systems. In the case of organic layers at the gold-solution interface, only neutrons can penetrate through the thick (80 mm in our case) substrate and probe the buried structure.

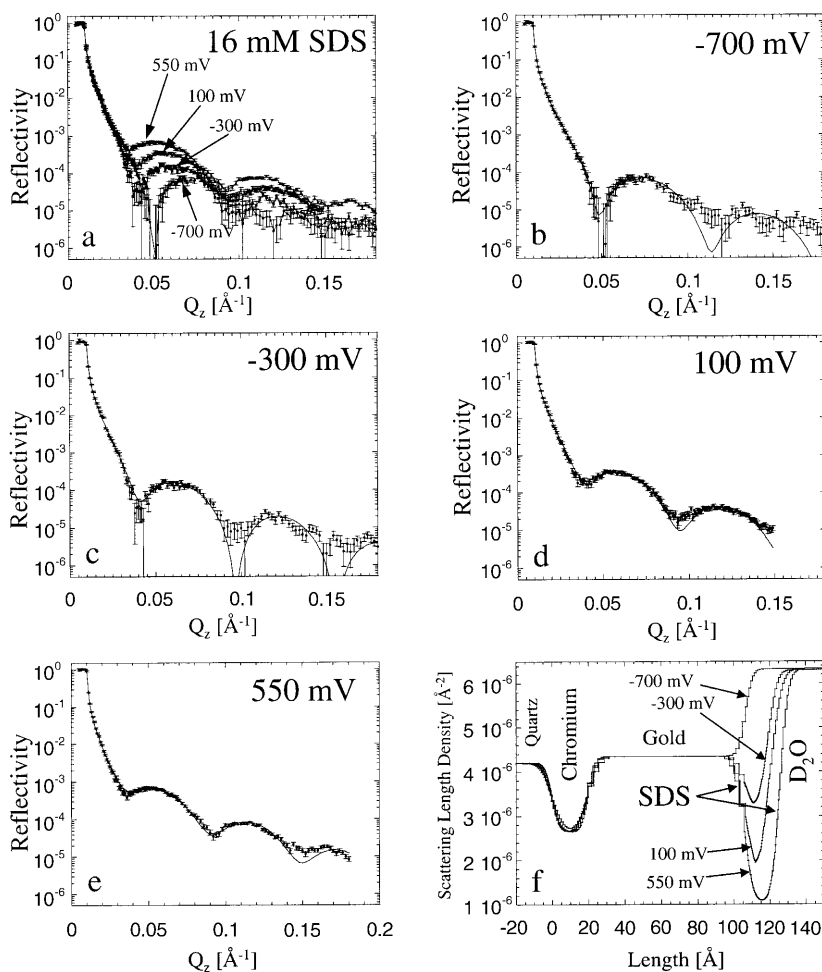


Fig. 2a–f. Normalized neutron reflectivity curves for a gold-coated quartz substrate in 16 mM SDS D₂O solution without supporting electrolyte. *Panel a* shows a progressive change of the reflectivity curves with the applied electrode potential. *Panels b* to *e* show individual reflectivity curves and best fits to the reflectivity data. *Panel f* shows the scattering length density profiles of the interface as determined from the fitting procedure

Table 1. Best-fit parameters for the modified quartz substrate (working electrode) in a 16 mM SDS in D₂O solution

| | SDS Layer | | Gold Layer | | Chromium Layer | | Roughness | χ^2 |
|---------|---|---------------------------|---|---------------------------|---|---------------------------|--------------------------|----------|
| | Scattering Length Density 10^{-6} \AA^{-2} | Thickness \AA | Scattering Length Density 10^{-6} \AA^{-2} | Thickness \AA | Scattering Length Density 10^{-6} \AA^{-2} | Thickness \AA | σ \AA | |
| −700 mV | — | — | 4.35(0.03) | 86.4(1.0) | 2.65(0.04) | 20.0(1.1) | 3.2(0.8) | 2.36 |
| −300 mV | 3.13(0.06) | 13.2(0.5) | 4.35(0.03) | 86.4(1.0) | 2.65(0.04) | 20.0(1.1) | 4.1(0.5) | 2.72 |
| | | | (fixed) | (fixed) | (fixed) | (fixed) | | |
| 100 mV | 1.36(0.1) | 13.7(0.3) | 4.35(0.03) | 86.4(1.0) | 2.65(0.04) | 20.0(1.1) | 5.1(0.2) | 2.67 |
| | | | (fixed) | (fixed) | (fixed) | (fixed) | | |
| 550 mV | 1.06(0.07) | 19.8(0.4) | 4.35(0.03) | 86.4(1.0) | 2.65(0.04) | 20.0(1.1) | 3.7(0.2) | 3.70 |
| | | | (fixed) | (fixed) | (fixed) | (fixed) | | |

2 Results

The reflectivity measurements in the presence of SDS were performed for several electrode potential, Fig. 2. The reflectivities were analyzed using the iterative, dynamic method [15]. Based on known facts about the system (fixed thickness of the gold and chromium layers to the values obtained from the X-ray scattering and possible structure of the organic layer at the interface), a model reflectivity profile was generated and minimized with the least squares fitting routine. Figure 2 shows the reflectivity curves measured in 16 mM SDS solution in D₂O without supporting electrolyte. By moving the potential from the negative limit to the positive direction we observe a progressive adsorption of SDS and a significant increase of neutron reflectivity. The scattering length density profiles calculated from these fits are shown in panel f and the parameters characterizing the film properties are summarized in Table 1. Similar experiments were also performed for 0.5 mM SDS solution with 50 mM KClO₄ as the supporting electrolyte (data not shown).

3 Conclusions

The results from neutron experiments are consistent with the electrochemical data. For the hemimicellar film the thickness of the hydrogenated layer varies between 13.7 and 15.3 Å. For the condensed film the thickness ranges from 19.8 to 21.3 Å. The surface occupancy by the hydrogenated species is around 75%. This data indicate that the film incorporates quite a significant amount of the solvent. The Gibbs excess data determined from our electrochemical experiments show that the surface concentration of SDS is doubled by crossing the phase transition and attains a value of $8.1 \times 10^{-10} \text{ mol cm}^{-2}$ in the condensed state. Such an increase of the surface concentration of the surfactant suggests the possibility of a bilayer formation. However, neutron reflectivity experiments indicate that the thickness of the condensed film is much less than the length of two fully stretched out SDS molecule and hence is consistent with the thickness of a monolayer rather than a bilayer film. For a monolayer, the surface concentration equal to $8 \times 10^{-10} \text{ mol cm}^{-2}$ corresponds to the area per SDS molecule in the film 20.7 \AA^2 . This number is essentially equal to the cross sectional area of the hydrocarbon tail of the SDS molecule. It indicates that in the condensed film, the hydrocarbon tails of the SDS molecules

are closely packed. A very high packing density of negatively charged molecules may be accomplished only if the charge of the anionic polar heads is effectively screened by the counter charge on the metal. The charge density data indicates that a condensed film of SDS forms at positive charge densities close to $40 \mu\text{C/cm}^2$. Although, the charge density on the metal is large, it corresponds roughly to a half of the negative charge of the SDS molecules in the condensed state. If all SDS molecules in the condensed state were turned with the sulfate group toward the metal, their negative charge would not be effectively screened by the positive charge on the metal and the repulsive forces between the negatively charged polar head would disrupt the film. In this case, the energetically stable packing of SDS molecules can be accomplished only in an interdigitated film in which half of the sulfate groups are turned toward the metal and half toward the solution. The negative charge of the sulfate groups lying on the metal is now effectively screened by the positive charge on the metal of approximately the same absolute magnitude. The charge of the sulfate groups turned to the solution may be also screened by the positive counterions from the diffuse part of the double layer. This film is stabilized by van der Waals forces between closely packed hydrocarbon tails. In this model, the thickness of the hydrogenated layer should be somewhat larger than the length of the hydrocarbon tail of the SDS molecule and significantly lower than the thickness of a bilayer, consistent with the neutron reflectivity data. In order for the length of the hydrogenated layer to equal 19.8–20.5 Å, the SDS molecules oriented in opposing directions have to be shifted from one another. This shift creates a void space that may be filled by solvent molecules. The void space, created by the shift of the hydrocarbon chains, amounts to about 25% of the volume of the hydrogenated layer. This number is close to the occupancy of the film by solvent calculated from the scattering length density data.

References

1. A.W. Adamson: *Physical Chemistry of Surfaces* (John Wiley & Sons: New York 1990)
2. J. Swalen, D. Allara, D. Andrade, E.A. Chandross, S. Garoff, J. Israelachvili, T.J. McCarthy, R. Murray, R.F. Pease, J.F. Rabolt, K.J. Wynne, H. Yu: *Langmuir* **3**, 932 (1987)
3. E. Sackmann: *Science* **271**, 43 (1996)

4. M. Stelze, G. Weissmuller, E. Sackmann: *J. Phys. Chem.* **97**, 2974 (1993)
5. H.M. McConnel, T.H. Watts, R.M. Weis, A.A. Brian: *Biochim. Biophys. Acta* **864**, 94 (1986)
6. P. Chandar, P. Somasundaran, N.J. Turro: *J. Colloid Interface Sci.* **117**, 31 (1987)
7. S. Manne: *Progr. Colloid Polym. Sci.* **103**, 226 (1997)
8. I. Burgess, V. Zamlynny, G. Szymanski, J. Lipkowski, J. Majewski, G. Smith, S. Satija, R. Ivkov: *Langmuir* **17**, 3355 (2001)
9. V. Zamlynny, I. Burgess, G. Szymanski, J. Lipkowski, J. Majewski, G. Smith, S. Satija, R. Ivkov: *Langmuir* **16**, 9861 (2000)
10. D. Bizzotto, J. Lipkowski: *J. Electroanal. Chem.* **409**, 33 (1996)
11. D. Bizzotto, J. Lipkowski: *Progr. Colloid Polym. Sci.* **103**, 201 (1997)
12. T. Sagara, V. Zamlynny, D. Bizzotto, A. McAlees, R. McCrindle, J. Lipkowski: *Israel. J. Chem.* **37**, 197 (1997)
13. I. Burgess, C.A. Jeffrey, G. Szymanski, Z. Galus, J. Lipkowski: *Langmuir* **15**, 2607 (1999)